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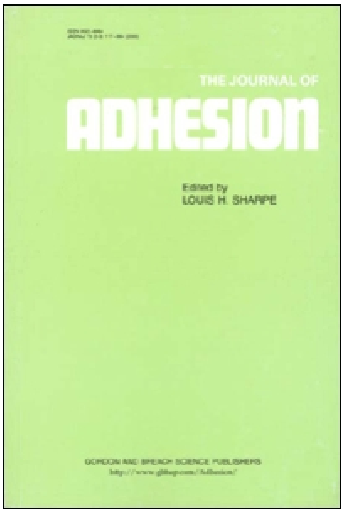

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End Group Effects on Adhesion of Perfluoropolyether Lubricants to Solid Substrates*

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Interfacial interactions of several commercial perfluoropolyether (PFPE) and aromatic-modified lubricants with silicon oxide or carbon substrates were investigated through contact angle measurement, dipping tests, fluorescence spectroscopy and contact-start-stop testing. All commercial lubricants that have not been thermally treated are displaced from the solid substrate by contact with water. Contact angles of water on ZDOL, a PFPE doubly-terminated with hydroxyl groups, spun on silicon and carbon-coated wafers were measured as a function of thermal annealing treatment. The adhesion of commercial lubricants to such previously thermally-bonded layers is stronger than to the bare silicon wafers. The thermal reaction of ZDOL on silica gel and carbon was investigated by thermogravimetric analysis and FTIR. The thermal reaction takes place when the baking temperature exceeds 70°C; at least part of this surface-bonding involves condensation of terminal hydroxyl groups with isolated surface silanols. Finally, stiction values for aromatic-modified lubricants are substantially lower than for the unmodified commercial PFPE lubricants, but there are still significant humidity effects.

Keywords: Perfluoropolyether (PFPE); disk lubricant; PFPE adhesion; end group effects; interface; aromatic-modified lubricant

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INTRODUCTION

The lubricant is a key component in magnetic disk technology. Its role is to minimize friction between the head and disk and to protect the medium from wear caused by direct head-to-disk contact [1]. In general, the lubricant is non-replenishable, or replenishable to only a limited extent, so that its loss by any mechanism, such as desorption, spin-off, or chemical degradation, is catastrophic. The perfluoropolyethers (PFPEs), which have been widely and successfully used as magnetic disk lubricants, are liquid oligomers exhibiting the necessary technological requirements including chemical inertness, oxidative resistance, thermal stability, low surface tension, relatively high molecular weight, low vapor pressure, good viscosity index and good lubricity. One technological disadvantage of the PFPE materials, however, is that they can be displaced by water, with the phenomenon being particularly sensitive to the type of PFPE end groups and any thermal treatment to which the disk has been subjected.

We have previously examined Langmuir and Langmuir-Blodgett films of several PFPE materials having two, one, or no surface-active terminal groups [2, 3]. Surface pressure isotherms on water show good surface activity with higher collapse pressures for the carboxy-terminated PFPE compared with hydroxy-terminated PFPE; trifluoromethyl-terminated materials are not surface active. Moreover, the doubly-terminated PFPEs are more expanded and show higher collapse pressures than the singly-terminated PFPEs. A thermodynamic analysis of the pressure-area isotherm below collapse suggests that there is no significant entropic contribution of the PFPE polymer chains to the equation-of-state behavior, and that the PFPE terminal groups act as a non-interacting "ideal gas" at the air water interface.

The PFPE monolayer studies clearly show the strong tendency of the hydrophilic terminal groups to interact with water. However, the adhesion of the PFPE materials to solid substrates used for magnetic recording may also depend upon a variety of other factors, including the possibility of covalent bond formation between the lubricant and the disk as well as the possibility that intermolecular interactions between other types of terminal groups could act to stabilize them on the solid surface. This issue has been addressed recently by several groups [4-9]. To explore this feature of molecular structure, we examine a range of commercial lubricants with and without functional end groups. We take advantage of the fact that the hydroxy-terminated materials may be easily esterified to allow attachment of dansyl or pyrene aromatic species. Such aromatic chromophores can exhibit polar and aromatic pi–pi interactions with surfaces as well as with each other, which may influence the interfacial behaviour of a modified PFPE containing such a group. We compare commerical PFPEs with these modified materials in a series of studies on resistance to water displacement, thermal annealing phenomena and static friction (stiction) measurements.

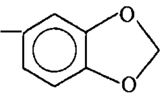
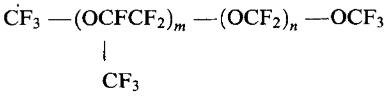
EXPERIMENTAL

Materials

Commercial Lubricants

Table I shows the various commerical PFPE lubricants examined in this study.

TABLE I Commercial PFPE lubricants

(1) Fomblin Z Lubricant (Montedison)			
$R-CF_2O-(CF_2CF_2O)_m-(CF_2O)_n-CF_2-R$			
R	*m/n*	*MW*	*Product Name*
$-CF_3$	0.6–0.7	8000	**Z15**
$-CH_2OH$	0.5–1.5	2000±400	**ZDOL**
$-CH_2-OCH_2-$ 	0.5–1.5	2000±400	**AM2001**
(2) Fomblin Y Lubricant (Montedison)			
 $CF_3-(O\underset{CF_3}{CF}CF_2)_m-(OCF_2)_n-OCF_3$		5500–7500	**YR**
(3) Demnum Lubricant (Daikin)			
$F-(CF_2CF_2CF_2O)_n-CF_2CF_3$		8400	**S200**
$F-(CF_2CF_2CF_2O)_n-CF_2CF_2CH_2OH$		3500	**SA**

Modified Lubricants

Dansyl-labeled ZDOL (ZDAN) Dansyl chloride (Aldrich), 2.7 g (0.01 mole), ZDOL, 9.2 g (0.004 mole), and triethylamine (Aldrich), 0.06 g (0.01 mole) were dissolved in 20 ml of a mixed solvent (2:3) of dichloromethane (Aldrich) and 1,1,2-trichloro-1,2,2-trifluoroethane (FC113) (Baker). The reaction mixture was refluxed for 4 h, filtered, and the solution was diluted with 75 ml of an aqueous solution of dilute hydrochloric acid (pH 4) and extracted with FC113. The extract was washed by an aqueous solution of dilute $NaHCO_3$ and then by water until pH 7 in the aqueous phase. The extract was dried over $MgSO_4$ and the solvent was evaporated. Purification [silica gel column, ether/FC113 (1:1)] provided 10.1 g of bright yellow liquid (yield 97%); IR (KBr): 2950, 2839 ($\nu_{C—H}$), 2794($\nu_{N—H}$), 1615 ($\nu_{S=O}$), 1200 (broad, $\nu_{C—F}$, $\nu_{C—O}$) cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$/FC113 (1:10)]: 7.8–8.4 (*m*, 12H, Ar–H)), 4.3 (*q*, 4H, OCH_2CF_2), 2.9 (*s*, 12H, NCH_3) ppm. The product was soluble in FC113 and weakly soluble in ether.

Dansyl-labeled Demnum SA (DASA) A process similar to the synthesis of ZDAN was used for the reaction of dansyl chloride with Demnum SA to obtain DASA. The yield was 67%. IR (KBr): 2953, 2840 ($\nu_{C—H}$), 2794 ($\nu_{N—H}$), 1615 ($\nu_{S=O}$), 1200 (broad, $\nu_{C—F}$, $\nu_{C—O}$) cm^{-1}; ^1H NMR [400 MHz, $CDCl_3$/FC113 (1:10)]: 7.2–8.7 (*m*, 6H, Ar–H)), 4.3 (*q*, 2H, OCH_2CF_2), 2.89 (*s*, 6H, NCH_3) ppm. The product was soluble in FC113 and weakly soluble in water.

Pyrene-labeled ZDOL (ZPY) Recrystallization of 1-pyrenebutyric acid (m.p. 184–186°C) was carried out in a mixed solvent (5:2) of ethyl alcohol and toluene (5:2). The acid chloride of pyrenebutyric acid was produced by the reaction of recrystallized pyrenebutyric acid, 1.44 g (0.005 mole), with thionyl chloride, 0.5 ml (0.0055 mole), in dichloromethane. The acid chloride was reacted with ZDOL in presence of triethylamine catalyst in a mixed solvent (1:1) of FC113 and dichloromethane. The mixture was refluxed for 8 h and then filtered. The solution was diluted by FC113, washed with an aqueous solution of dilute $NaHCO_3$ and then by water until the aqueous phase was pH 7. The organic phase was dried with Na_2SO_4 and the solvent was rotovapped. The solid product was purified using a silica gel column with a mixture (5:1) of FC113 and ether as eluent (yield 85%);

IR (KBr): 3044 (ν_{Ar-H}), 2953, 2850 (ν_{C-H}), 1762 (ν_{COO}), 1604 ($\nu_{C=C}$), 1200 (broad, ν_{C-F}, ν_{C-O}) cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$/FC113 (1:10)]: 7.8–8.3 (*m*, 18H, Ar–H)), 4.5 (*q*, 4H, OCH_2), 3.4 (*t*, 4H, $ArCH_2$), 2.6 (*t*, 4H, CH_2COO), 2.2 (quintet, 4H, CH_2) ppm; m.p. 35–38°C. The solid product was soluble in FC113 and weakly soluble in ether.

Pyrene-labeled Demnum SA (PYSA) PYSA was obtained by the reaction of pyrenebutyric chloride with Demnum SA in a procedure similar to the ZPY synthesis. IR (KBr): 3403 (ν_{Ar-H}), 2953, 2879 (ν_{C-H}), 1761 (ν_{COO}), 1604 ($\nu_{C=C}$), 1363, 1315, 1234 (broad, ν_{C-F}, ν_{C-O}) cm^{-1}; ^{1}H NMR [400 MHz, $CDCl_3$/FC113 (1:10)]: 7.8–8.3 (*m*, 9H, Ar—H)), 4.54 (*t*, 2H, OCH_2), 3.41 (*t*, 2H, $ArCH_2$),. 2.53 (*t*, 4H, CH_2COO), 2.23 (quintet, 2H, CH_2) ppm; m.p. 39–45°C. The solid product was soluble in FC113 and weakly soluble in ether.

Substrates and Thin Films

One-inch diameter quartz and silicon wafers having sputtered 250 Å thick carbon coatings were obtained from IBM Almaden Research Center. The amorphous hydrogenated carbon coating (a—C:H) was deposited by DC magnetron sputtering in a hydrogen/argon atmosphere at a rate of 3 to 5 Å/sec. Surface roughness is approximately 40 nm rms. The bulk elemental composition is approximately 25% hydrogen, and the top surface of the carbon coating contains about 20% oxygen. The predominant chemical species on the surface are carboxyl and hydroxyl, with some additional carbonyl groups [5]. The coating is conformal to the thin film magnetic substrate. They were cleaned by immersion in FC113, placed in FC113 vapor for 20 m, and finally rinsed three times with deionized water and dried at 50°C under nitrogen ambient. Two-inch silicon wafers obtained from the Stanford Center for Integrated Systems were cleaned by immersion in 9:1 H_2SO_4:H_2O_2 solution at 120°C for 30–60 m, followed by at least six rinses with deionized water and a final drying at 150°C under nitrogen ambient or in air.

The lubricant thin films were prepared by spin-casting of dilute lubricant solutions in FC113 (approximately 1 mg/ml) at 8000 rpm for 60 s. After spinning, the films were dried at 50°C for 30 m in air to evaporate the residual solvent. Higher temperature baking of the thin films was performed under nitrogen or in air. Film thicknesses were measured by a Gaertner ellipsometer, with experimental error approximately ±2 Å. No information on pinhole density is available, but such pinholes might be expected for ultrathin films less than 100 Å thick.

In order to have sufficient interfacial area to study thermal treatment effects on possible surface bonding reactions between the PFPE lubricant and the solid substrate, two complementary experiments with particulate material having qualitatively similar surface chemistry to the planar substrates were carried out. In the first, silica gel H, supplied by E. Merck (Germany), was prebaked at 700°C in air for 4–8 h and then cooled to room temperature. 8.6 g ZDOL was dissolved in FC113, mixed with 4.1 g silica gel (2.1:1 = w:w of ZDOL:silica gel) and dried in air at room temperature. The mixture was baked at various temperatures for 40 m and then rinsed several times with FC113 until no ZDOL was detected in the eluent by FTIR. In the second experiment, activated carbon (Baker) was prebaked at 400°C in air for 5 h and then mixed with ZDOL (2.1:1 w:w of ZDOL/carbon. Both sets of particulate/ZDOL samples were then examined with ThermoGravimetric Analysis (TGA).

Characterization Techniques

Water contact angles (±2°) were measured on a Ramé-Hart contact angle goniometer using the same volume of water for each measurement. Front-face, corrected fluorescence spectra were measured on a SPEX 212 FLUOROLOG spectrofluorometer (2.0 mm slits) equipped with a 450 W Xenon lamp and SPEX DM1B data acquisition station. TGA analysis was done on a DuPont 2100 TGA in an argon gas environment with the temperature ramped up at 10 C/m. A Perkin-Elmer 1710 FTIR spectrometer, equipped with a DTGS detector, was used to monitor the reaction products and to follow the thermal annealing of the silica gel and carbon.

The tribological experiments were performed with a contact-start-stop tester of an early design that was fabricated at IBM Almaden Research Center. It consists of a modified Seagate 5-1/4 inch [12.7 cm] hard disk drive operating at 3600 rpm. An uncoated, dual-rail slider (100% slider having flat bottom with a slightly tapered tip) composed of N-58 hard ceramic (alumina calcia titanate prepared by sintering of aluminum oxide and titanium carbide) with a contact area of approximately 20 mm^2 was placed under a 15 gm load. Astro disks were used for all experiments.

RESULTS AND DISCUSSION

Water Displacement of Lubricant for Un-annealed Films

Contact angles of water droplets placed on PFPE lubricant films coated on various substrates are listed in Table II. For a particular lubricant, the contact angle appears to depend upon the substrate, contrary to expectation. Moreover, for a particular substrate, it is also clear that the contact angle depends on the type of lubricant. For example, the value for AM2001 on the silicon wafer is 36°, while the value for ZDOL is just 24°, even though they have the same polymer backbone and molecular weight and were spun at the same speed and concentration. Since the contact angle is generally believed to be sensitive to only the outer 5 to 10 Å of the film, these results suggest that the water test fluid may be displacing the lubricant from the substrate, thereby exposing a more hydrophilic surface. To test this, we monitored the contact angle as a function of the residence time of the water droplet on the films for Demnum SA and its dansyl-modified derivative, DASA, as shown in Figure 1. Both showed significant decreases in contact angle during the experiment, suggesting that lubricant displacement was, indeed, occurring.

An empirical test designed to assess qualitatively the extent of interaction between the lubricant and a substrate is a dipping test, also performed on lubricant coatings that had not received any thermal

TABLE II Contact angles of water on lubricant films spin-cast on various substrates. The spin-casting was performed at 8000 rpm

Lubricant	*bare substrate*	*AM2001*	*ZDOL*	*Demnum SA*	*S200*	*YR*	*Z15*	*DASA*	*ZDAN*
GLASS	30°	55°	54°	~	50°	45°	45°	~	~
Si/SiO$_2$	5	36	24	33	19	18	22	40°	38°
CARBON	65	87	87	90	68	71	68	91	87

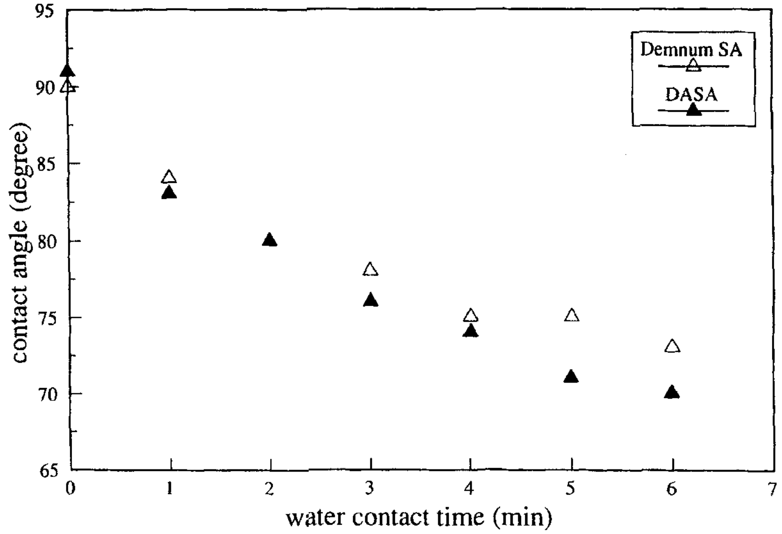


FIGURE 1 Contact angle of water on Demnum SA and DASA films as a function of the contact time of the water droplet with the film.

treatment. The lubricant film prepared by spin casting at 8000 rpm was dipped into and removed from deionized water at a speed of 70 mm/s at room temperature for five cycles, leading to a considerable reduction of the film thickness, as shown in Table III. Two qualitative observations may be made from these data. First, almost all commercial lubricants examined (AM2001, ZDOL, S200, YR and Z15) can be completely displaced from silicon wafers, while they are only partially displaced from carbon wafers. Second, the aromatic-

TABLE III Effect of water dipping test on spin-cast lubricant films

Substrate	*Si/SiO$_2$*		*Carbon*	
Lubricant	*No Dipping*	*Dipped*	*No Dipping*	*Dipped*
AM2001	65±2 Å	2±1 Å	88±5 Å	13±5 Å
ZDOL	43±2	2±1	75±5	12±5
Demnum SA	47±2	5±1	90±5	36±5
S200	42±2	2±1	103±5	60±5
YR	69±2	2±1	135±5	85±5
Z15	32±2	2±1	92±5	59±5
DASA	40±2	35±2	53±5	36±5
ZDAN	44±2	13±2	47±5	33±5

modified lubricants exhibit greater resistance to water displacement than their unmodified complement, e.g. DASA is more resistant than Demnum SA and ZDAN is more resistant than ZDOL. Both sets of observations may be related to the increased number of types of intermolecular interactions possible with the amorphous hydrogenated carbon surface.

The displacement in the dipping experiment was also monitored by the fluorescence spectra of AM2001, which contains piperonyl chromophores as the terminal groups, as well as by fluorescence from dansyl groups on ZDAN. The maximum emission band of AM2001 is at 315 nm, while the dansyl group emits at about 480 nm in a nonpolar medium. The emission intensity decreased with the dipping, as shown in Figure 2, with the process occurring more rapidly for the AM2001 than for the ZDAN, from which we infer that the dansyl chromophore interacts slightly more strongly with the wafer surface than does the piperonyl group, possibly due to the increased polarity of the dansyl

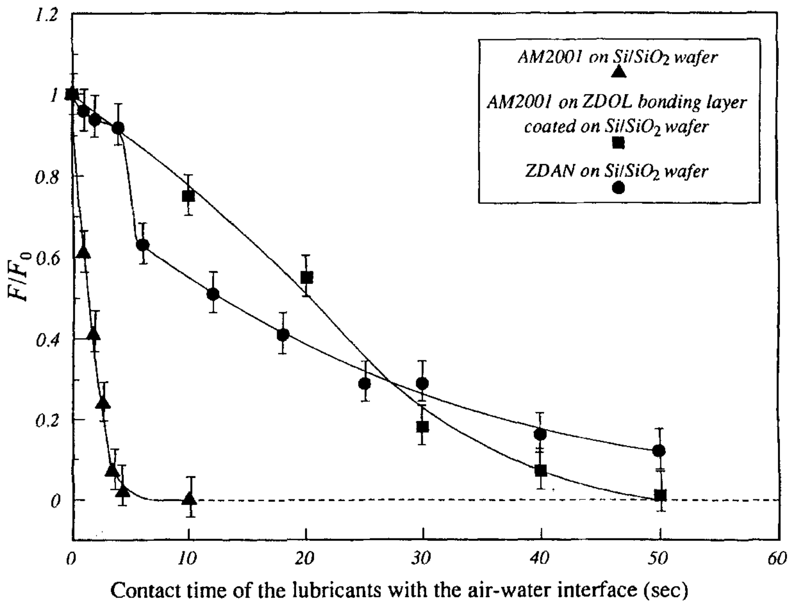


FIGURE 2 Ratio of fluorescence intensity of AM2001 and ZDAN films with the dipping (F) to that without the dipping (F_0) for different substrates as a function of the contact time of the films with the air–water interface.

group compared with the piperonyl group. Nevertheless, lubricant is being lost from the silicon wafers in both cases.

The fluorescence intensities of AM2001 film on the silicon wafer were also measured when the lubricant-coated substrate was rapidly immersed into the water and kept below the water surface. Interestingly, there was only a slight decrease of the fluorescence intensity after the film had been immersed in water for times between 1 m and 20 m. However, after this film was pulled out and dipped into the water again, a significant reduction in fluorescence intensity was detected. This indicates that the displacement of the lubricant by the water does not easily take place in the water phase, but is facile at the air – water interface.

Effect of Thermal Treatment on Interfacial Properties

The contact angles of water on ZDOL baked at different temperatures for 30 m are given in Figure 3. The temperature corresponding to the abrupt change of contact angles with increasing baking temperature is

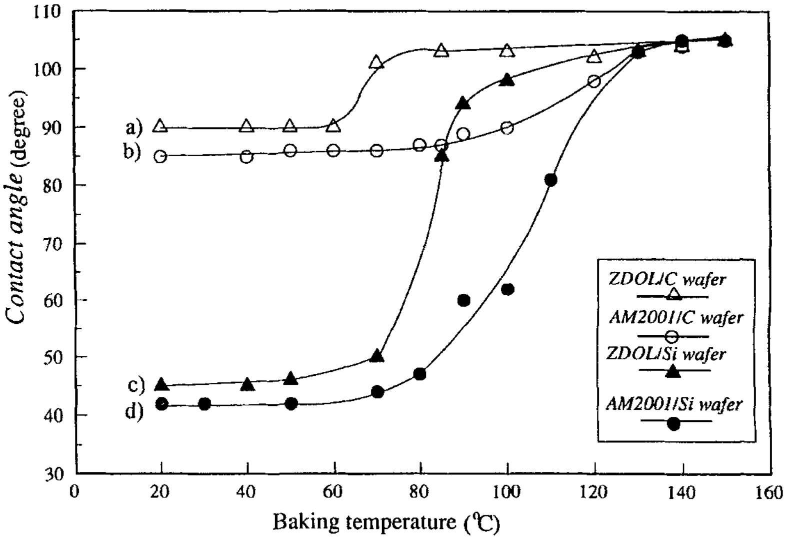


FIGURE 3 Contact angle of water on ZDOL film coated on silicon and carbon wafers as a function of baking temperature.

defined as the critical temperature (T_c). This appears to be dependent upon the nature of the terminal group, with values of approximately 65°C for the hydroxy-terminated ZDOL and approximately 85°C for the piperonyl-terminated AM2001. Prior to baking, or for baking at temperatures below T_c, the contact angle remained constant at 107° for both ZDOL and AM2001 and for both substrates. Upon rinsing by FC113, the film thickness decreases for both ZDOL and AM2001, with the thickness of the residual film being approximately 10 Å. This residual ZDOL film can function as a "bonding layer" to enhance the adhesion of AM2001, as shown in Figure 2.

However, no such residual film remains for S200, YR and Z15 films, which can be completely washed away by FC113 and water, even if the films were baked at 150°C for 30 m.

In actual disk file operation, the temperature within the device is of the order of 45 to 60°C [8]. As such, it is of interest to examine the thermal characteristics of the aromatic-modified lubricants because the terminal groups on the commercial AM2001 and the modified ZDOL (ZDAN and ZPY) as well as Demnum SA (DASA and PYSA) might be expected to associate or even crystallize. This might subsequently have an effect on the tribological properties. In fact, none of the commercial lubricants is a solid at room temperature. Figure 4 presents DSC data in which a single low temperature transition commences at −111°C for ZDOL and −109°C for Demnum SA; this is assigned to the glass transition for these highly flexible materials. Similar glass transitions are observed for the pyrene-modified ZPY and PYSA but, in addition, a strong melting endotherm was observed with peak temperature values of approximately 39°C and 52°C, respectively, which are consistent with the separately determined melting temperatures. Presumably, this is a result of interactions between the terminal aromatic groups.

In order to understand the influence of the thermal treatment on the lubricant depletion upon rinsing with water, we first examined the thermal stability of the lubricant itself. To do so, we heated ZDAN, DASA, ZPY and PYSA samples at 150°C for 24 h and observed that the ^{1}H NMR and FTIR spectra did not change. The TGA analysis in Figure 5 shows that the commercial ZDOL and Demnum SA start degrading at about 150°C, with half-weight-loss temperatures of about 310°C and 400°C, respectively. However, degradation of ZDAN and

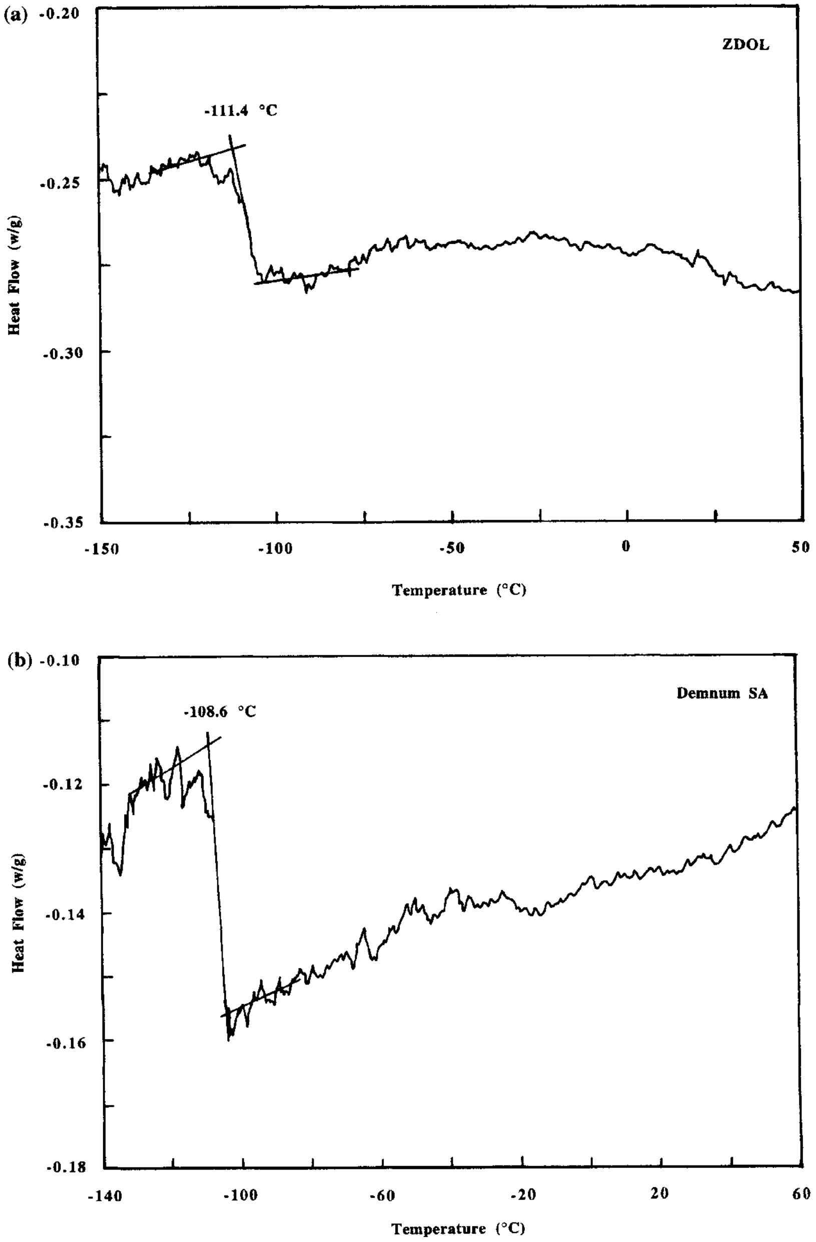


FIGURE 4 Differential scanning calorimetry results for (a) ZDOL, (b) Demnum SA, (c) ZPY and (d) PYSA.

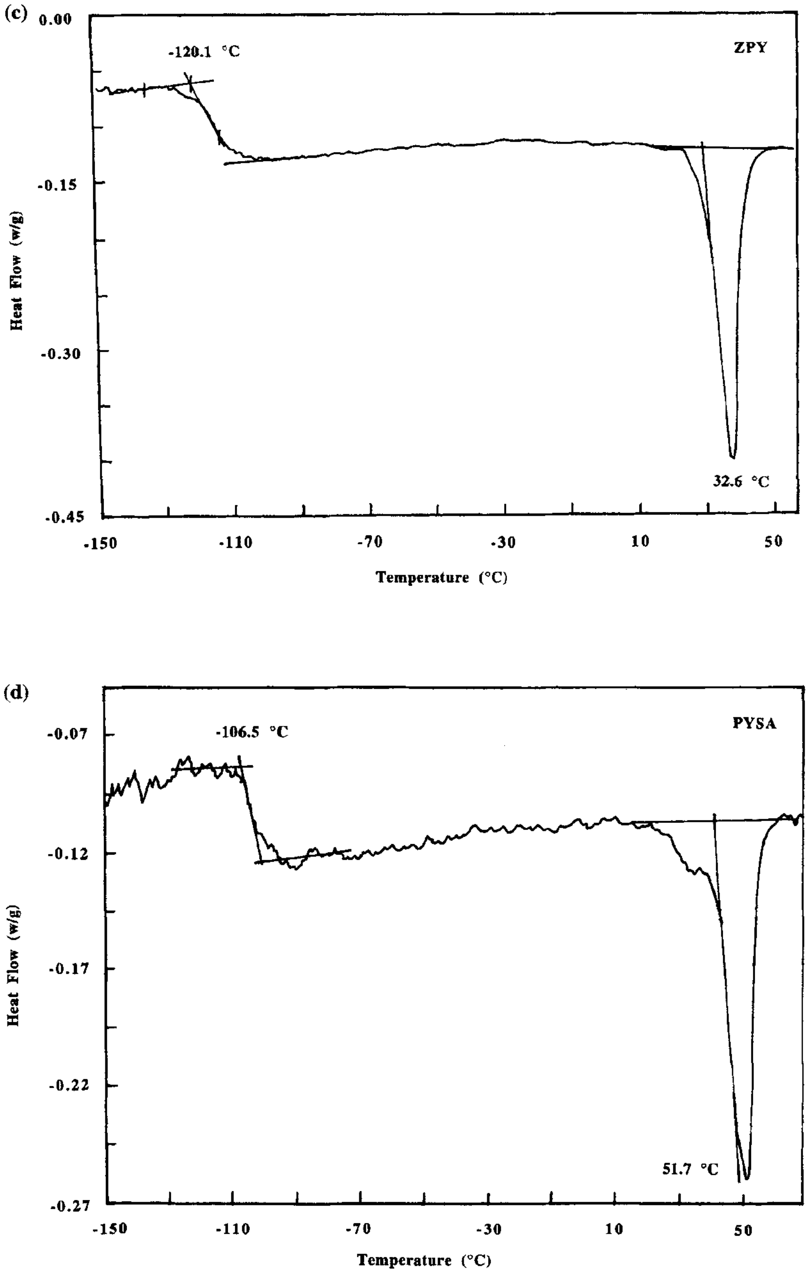


FIGURE 4 (Continued).

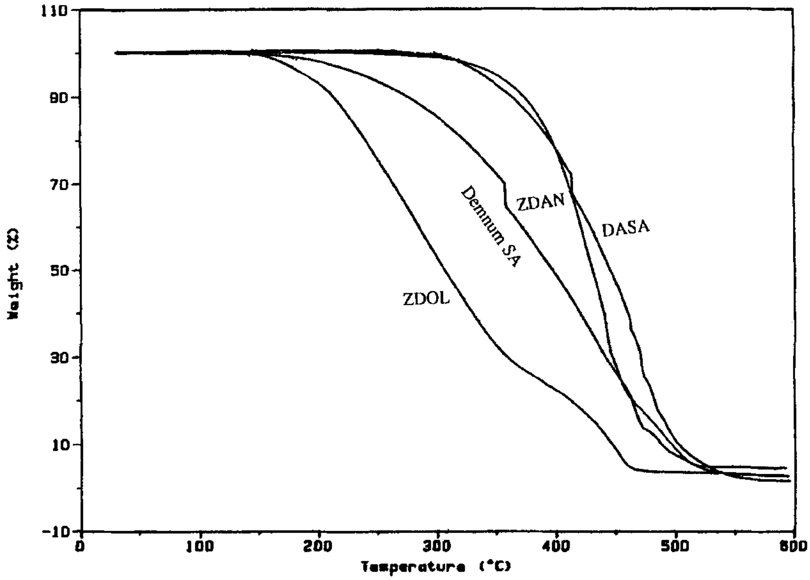


FIGURE 5 Thermogravimetric results for ZDOL, Demnum SA, ZDAN, and DASA.

DASA does not begin until 320°C, with half-weight-loss temperatures of 440°C and 450°C, respectively. Corresponding data for ZPY and PYSA (not shown) indicate that thermal degradation does not occur until 300°C, with half weight loss temperature of 420 and 390°C, respectively. The modified lubricants clearly have higher thermal stability than the corresponding commercial PFPEs. Nevertheless, since both ZDAN and DASA can be rinsed off by FC113 even after baking, they must not be chemically bonded to the substrate. Comparable data are unavailable for ZPY and PYSA, but these should give comparable results because they have no polar groups and could only interact with the surface through pi–pi dispersive interactions.

To explore the possibility that the hydroxy-terminated ZDOL chemically reacts with the silica surface, we have examined thermal treatment of mixtures of ZDOL and silica gel, which has a large surface area and may have approximately the same surface chemistry as the oxidized wafer surface. TGA data for materials prepared as described in the Experimental section are shown in Figure 6. As a

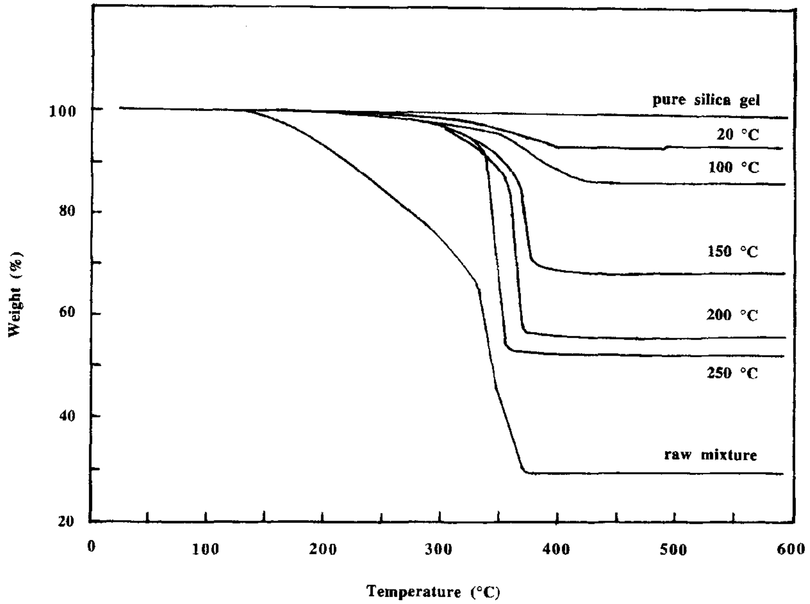


FIGURE 6 Thermogravimetric results for a mixture of ZDOL and silica gel baked at various temperatures: (1) pure silica gel, (2) the mixture without baking or rinsing. The remaining mixtures were baked at different temperatures and then rinsed with FC113: (3) 20°C, (4) 85°C, (5) 100°C, (6) 150°C, (7) 200°C, (8) 250°C.

reference, Curve 1 shows that the weight loss of the pure silica gel is only 1% at 600°C, which is attributed to loss of absorbed water. By comparison, Curve 2 is the result for the mixture of ZDOL and silica gel without any baking or rinsing with FC113. Two transition temperatures are observed: one is near 150°C and the other appears at about 330°C. The lower transition temperature is identical to the initial weight loss temperature of pure ZDOL shown in the TGA curves of Figure 5, and is assigned to loss of physisorbed ZDOL, whereas the higher temperature may reflect chemical degradation of the ZDOL.

After the mixture of ZDOL and silica gel is baked, the remaining ZDOL that cannot be washed away with FC113 is assumed to be chemically bonded to the silica gel surface. Curves 3–8 in Figure 6 were obtained by first baking at the temperatures stated and then rinsing several times with FC113 until no ZDOL was detected in the rinse solvent by FTIR. When these samples are subsequently heated to temperatures higher than 330°C, chemical degradation becomes rapid and the ZDOL is volatilized. Thus, an estimate of the amount of ZDOL that had been chemisorbed on the silica gel as a result of the thermal treatment may be obtained from the final weight losses of the mixtures. These plateau data are shown in Figure 7. When the baking temperature is below 70°C, the weight loss is small because there is very little ZDOL that is chemically bonded to the silica gel. The amount of ZDOL attached to the surface is about that determined for the raw material without baking and remains constant to a baking temperature of 70°C; for higher baking temperatures weight loss increases up to 250°C. These results demonstrate that thermal bonding does not begin until baking temperatures above 70°C, consistent with the contact angle results of Figure 3. TGA data for ZDOL on carbon are similar to the results for silica gel. However, Figure 7 shows that the amount of material chemisorbed on the carbon is considerably less, even though the results of the dipping experiments suggest that there is stronger physisorption to the carbon surface.

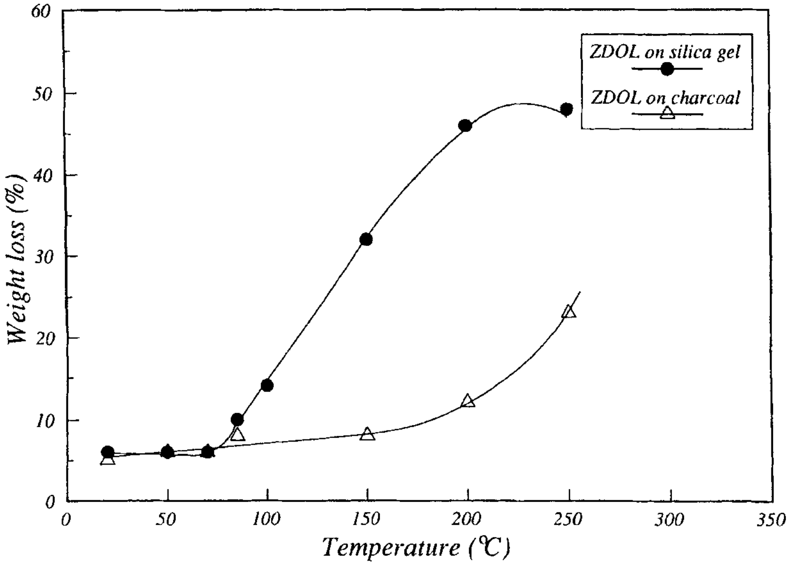


FIGURE 7 The weight loss of ZDOL bonded on silica gel and charcoal as a function of the thermal treatment temperature.

The surface of silica gel consists of siloxane bridges between tetravalent silicon atoms in the presence of geminal, vicinal, and isolated silanol groups, which provide bonding sites. When silica gel is heated in vacuum, absorbed water is removed first; at temperatures above 250°C, the concentration of physisorbed water is negligible. As the temperature is increased above this point, the number of silanols is reduced from 6/100 $Å^2$ to approximately 2/100 $Å^2$ at 500°C and 1/100 $Å^2$ at 800°C [10]. In the temperature range of 500 to 700°C, the number of geminal silanol groups remains roughly constant, but the regeneration of silanols by exposure to water vapor decreases rather suddenly. Thus, heating the silica gel above 500°C followed by rehydration changes the proportion and distribution of isolated silanol sites. At higher temperatures, only isolated silanol groups exist. Since the FTIR absorption band at 3751 cm^{-1} (data not shown) for isolated silanol groups still exists after the silica gel physisorbed the ZDOL, but disappears when the mixture is baked at 150°C, we conclude that at least some of the ZDOL is reacting with isolated silanol groups on the surface during the baking.

Tribological Experiments

We present tribological Contact-Start-Stop (CSS) test data only for the pyrene-labeled PFPEs, as representative of the class of aromatic modified lubricants. For comparison, we also examine the properties of the corresponding commercial lubricants. Figure 8 shows the lubricant weight loss for PYSA and Demnum SA on the hard disk as a function of the spin-off time. No thermal treatment was used for either material. There is a 40% weight loss and a significant decrease of the film thickness (from 91 to 57 Å) for Demnum SA after 770 h spinning. However, only 5% weight loss and a small thickness change (approximately 5 Å) of the PYSA occurred after the same spinning time. We attribute the higher retention time of PYSA on the substrate both to crystallization of the pyrene terminal groups as well as to the relatively strong physisorption of the PYSA to the substrate.

Since most commercial disk drives spin up to rotation with the heads sitting on the disk surface, PFPE lubricants are designed to eliminate the static friction, referred to as "stiction" between the PFPE

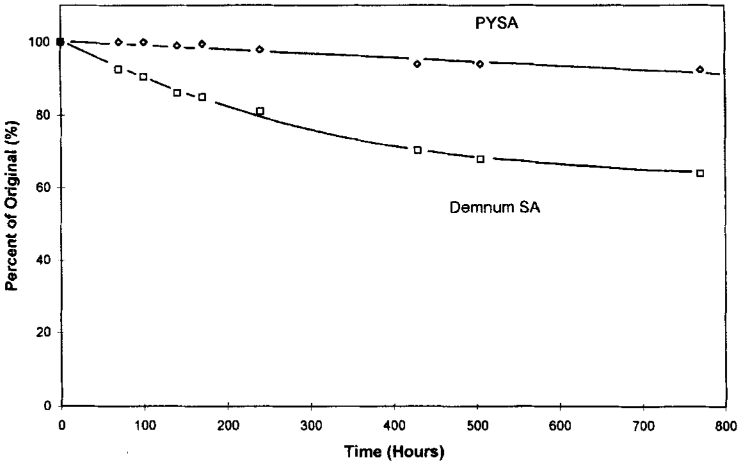


FIGURE 8 Lubricant weight loss as a function of disk spin-off time for PYSA and Demnum SA.

coated hard disk and the magnetic read/write head during this start-up sequence. Normally, the static friction is due to the work required to make and break contact in the head/disk space. When the lubricant thickness reaches a critical value t_c, however, the stiction abruptly increases with increasing lubricant thickness. The t_c increases on a rougher or more porous surface, and decreases in a higher humidity environment. Thus, the lubricant quantity is set to be just below t_c in a typical manufacturing protocol.

The stiction of Demnum SA, ZDOL, PYSA, and ZPY lubricants as a function of the film thickness is presented in Figure 9. The average stictions of 20-cycle CSS tests on the commercial Demnum SA and ZDOL rapidly increase when the lubricant film thicknesses are greater than 20 Å, while the stictions on PYSA and ZPY lubricants are almost constant for film thicknesses over the range of 0 to 50 Å. It appears that the t_c values of PYSA and ZPY must be larger than those of Demnum SA and ZDOL.

The stiction is also influenced by the humidity. If water is present at the interface, its high surface tension creates a high stiction. Figure 10 displays the stiction on a 50 Å ZPY film as a function of CSS cycles. When the experiment is carried out in a chamber at 80% relative humidity, the stiction increases up to quite large values. However,

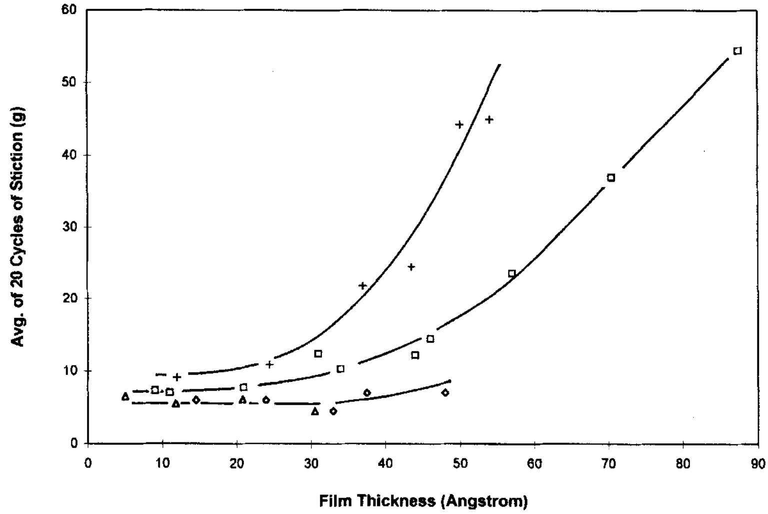


FIGURE 9 Stiction of Demnum SA(+), ZDOL (□), PYSA (Δ), and ZPY (◇) as a function of film thickness.

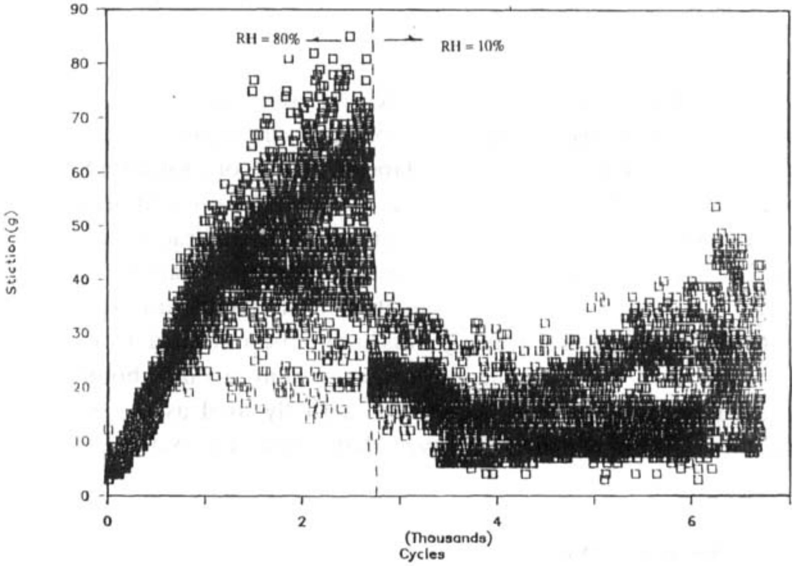


FIGURE 10 Effect of humidity on stiction for a ZPY film.

when the ambient atmosphere was changed to a 10% relative humidity value, the stiction recovered to a significantly lower value.

CONCLUSIONS

We have presented a wide range of experimental results that demonstrate the importance of the end-group on the adhesion of PFPE lubricant materials to silicon dioxide or carbon surfaces. Contact angle and dipping tests show that PFPEs with $—CF_3$ terminal groups (S200, YR, Z15) are rather easily displaced from solid substrates by water, i.e. water wets the surface in preference to the PFPE lubricant. Although the interaction with the surface is stronger for commercial lubricants with hydroxyl (ZDOL, Demnum SA) or piperonyl (AM2001) end groups, they too are displaced by water if they are not thermally treated. However, thermal treatment has a significant influence on the adhesion of ZDOL to the solid surface. We observed that the surface-bonding reaction, presumably a condensation between a surface silanol and a terminal hydroxyl group, begins at about 70 °C and continues up to temperatures around 250°C, after which chemical degradation of the ZDOL backbone becomes increasingly important.

The aromatic-modified PFPEs are interesting materials. Compared with the unmodified commercial lubricants, the surface interaction is stronger for the dansyl or pyrene-labeled ZDOL or Demnum SA. This may be due to the fact that dansyl group provides possibilities of polar interactions, hydrogen bonding, and aromatic interactions with the surface. In addition, the pyrene group appears to exhibit a crystallization phenomenon, which might lead to temperature-dependent tribological properties, although this has not been studied. Comparison of substrates shows that the lubricants are more strongly bound to the carbon surface, which is the surface actually used as the protective overcoat in commercial disk drives, than to the silicon dioxide.

Acknowledgement

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